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CENTRAL FILES NUMBER
73-4-31

DATE: April 26, 1973

SUBJECT: Progress Report on Development Work Associated with Waste Disposal by Hydraulic Fracturing for Period Ending March 31, 1973

TO: R. E. Blanco

FROM: H. O. Weeren and J. G. Moore

ABSTRACT

This is a progress report on the development work associated with radioactive waste disposal by hydraulic fracturing.

Grout leach studies are in progress to determine the effect of grout curing time on the leach rates of cesium and strontium. The maximum effective diffusivity that was determined for cesium is 1.8×10^{-3} cm^2/day, 3.1×10^{-4} cm^2/day, and 6.8×10^{-6} cm^2/day for 0, 7, and 28 day cured specimens. For strontium the respective values are 2.6×10^{-3} cm^2/day, 2.3×10^{-4} cm^2/day, and 1.2×10^{-7} cm^2/day.

A proposed design refinement for the new shale fracturing facility would be the elimination of the waste pit, if the grout washed from the facility during cleanup could be kept pumpable until the next injection and injected at this time. Tests indicated that a grout that is well stirred with an excess of water for 24 hrs forms a fine silt that can be resuspended easily weeks afterwards.

An estimate of the magnitude of loss of radionuclides from well dispersed grout was determined. A maximum of 6% of the cesium and 2% of the strontium was lost under these conditions.

The first draft of the environmental impact statement for the proposed new shale fracturing facility has been completed.

MIX DEVELOPMENT

Grout Leach Studies

Grout leach tests are in progress to determine the effect of curing time on the leaching of strontium and cesium from grouts made using 6 lb of standard solids per gallon of W-7 simulated waste. The initial data show that the leach rate varies inversely with curing time. In a series of duplicate experiments the average amount of the initial strontium leached from 100 cm^3 specimens in 35 days was 5.4%, 1.4%, and 0.043% for 0-, 7-, and 28-day cured grouts, respectively. For cesium the values were 4.7%, 1.8%, and 0.40%, respectively, for the same curing periods.

Effective diffusion coefficients were calculated for both strontium and cesium for the first few weeks of leaching. The leach factors were constant for about the first 3 weeks and then began to decrease. Thus, the maximum effective diffusivity for cesium was 1.8×10^{-3} cm^2/day, 3.1×10^{-4} cm^2/day, and 6.8×10^{-6} cm^2/day, respectively, for 0-, 7-, and 28-day cured specimens. For strontium the respective values were 2.6×10^{-3} cm^2/day, 2.3×10^{-4} cm^2/day, and 1.2×10^{-7} cm^2/day. The leach tests followed the IAEA recommendations as closely as possible. Duplicate tests were made using cylindrical specimens 50 mm in diam and 50 mm high containing approximately 100 cm^3 of grout. The grout was prepared using the standard solids mix and W-7 simulated waste containing either ^{85}Sr or ^{137}Cs in trace quantities for analytical purposes. The specimens were cured in a humid atmosphere for the specified time then leached with 150 ml tap water. A surface area of 20 cm^2 was exposed to the leachant. The tap water was changed daily until the activity in the leachant was too low for accurate measurement then weekly changes were made. The tests are continuing to obtain data for determining the leach characteristics over longer periods of leaching.

Cesium Loss into Phase Separated Water

A grout containing ^{137}Cs was prepared at 4-1/2 lb/gal to determine the percentage of activity that would be present in the phase separated

water. There was about 2% phase separation and the water contained approximately 0.1% of the total cesium. The grout was prepared using 200 ml of W-7 simulated waste solution containing 1.8×10^5 c/m/ml ^{137}Cs. Sufficient dry mix was added to produce a grout with a solids/liquid ratio of 4-1/2 lb/gal to insure enough phase separation liquid to measure. The grout was next poured into two 100 ml graduates, allowed to stand 2 hr and the activity measured in the phase separated water.

Effect of Water in Keeping Waste Grout Dispersible

At the end of a waste disposal injection there often remains excess grout which must be eliminated. It would facilitate disposal if this grout were maintained in a state such that it could be mixed with fresh grout at a later date for injection during the next hydrofracture run. It was found that adding 20 volumes of water to a standard grout and mixing vigorously for 18 hr produced a silt-like material that was easily resuspended with stirring. The grout was prepared by mixing at 7 lb/gal, the standard dry mix with simulated waste solution W 9/10. This thick grout was then mixed with 20 vol of water by stirring vigorously overnight. After stirring, the grout settled in about 8 min as a silt or mud-like material with a clear supernate. It was resuspended easily by stirring with a magnetic stirrer even after being allowed to stand for about 3 weeks.

Loss of Cesium and Strontium from Freshly Prepared Grouts into Water

Information was required to assess the loss of activity to the aqueous phase if radioactive grout were dumped into a rapidly moving body of water. Grouts at 6 lb/gal were prepared with W-7 simulated waste containing either ^{137}Cs or ^{85}Sr then mixed 24 hr with either 3 vol or 10 vol of water. After settling, the activity in the supernatant liquid was measured and the total amount lost to the waste calculated. Approximately 4% and 6% of the cesium and 1% and 2% of the strontium was lost to the 3 vol and 10 vol of water, respectively. These losses to the aqueous should be considered as upper limits since part of the water mixed with the grout was incorporated into it as it solidified. In the 3 vol test,

after one week, less than about 1/3 of the water which had been added was present as supernate, the remainder was in the solid grout. Thus, less than about 1% of the cesium or 0.3% of the strontium was in the aqueous supernate. The experiment will be repeated using a shorter mixing period and increased concentrations of strontium to determine the effect of these variables on the loss of activity to the aqueous phase.

Environmental Impact Statement

The first draft of the environmental impact statement for the proposed new shale fracturing facility has been completed. Review and rewriting of this statement will follow. The scheduled completion date for the final version is July 1.

Previous reports in this series have been CF-72-8-39, CF-72-10-23, CF-72-11-9, CF-72-12-7, CF-72-12-32, and CF-73-2-42.

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OAK RIDGE, TENNESSEE 37830

DATE: February 28, 1973

SUBJECT: Monthly Progress Report on Development Work Associated with Waste Disposal by Hydraulic Fracturing

TO: R. E. Blanco

FROM: H. O. Weeren and J. G. Moore

SUMMARY

This is a report on the development work associated with radioactive waste disposal by hydraulic fracturing. Work is currently in progress in the areas of mix development and accumulation of data for a forthcoming impact statement.

Laboratory studies of the relative effect on grout viscosity of continuous as opposed to very discontinuous stirring (an effect of interest for the impact statement) showed little real difference.

A series of grout leach studies has been initiated. These studies are needed to update old data and to provide new data for the impact statement. A standard mix, a standard solution, and a standard procedure have been adopted and a problem safety summary has been issued. The loss of strontium from grouts in the phase separated water that is formed as the grout sets has been measured for one mix and found to be 0.018%. This is considerably lower than the 1% to 0.1% strontium loss that was determined early in the project.

MIX DEVELOPMENT

Grout Leach Studies

The problem safety summary for the grout leach studies has been written and approved. Tests are in progress to determine the effect of curing time on the leaching of strontium (^{85}Sr) from grouts made using 6 lb of standard solids mix per gal of W-7 simulated waste. The standard solids mix is made up as follows:

Cement (type 1) - 2.5 parts
Fly Ash - 2.5 parts
Attapulgite 150 drilling clay - 1.0 part
Illite - 0.5 part
Delta gluconolactone - 0.003 part

The W-7 simulated waste solution contains:

NaOH	- 0.18 M
$Al(NO_3)_3$	- 0.0074 M
NH_4NO_3	- 0.003 M
$NaNO_3$	- 0.81 M
NaCl	- 0.093 M
Na_2SO_4	- 0.094 M
Na_2CO_3	- 0.19 M

The last series of waste injections required solid/liquid ratios of at least 7 lb/gal; however, preliminary tests show that 6 lb/gal is about the maximum that can be handled easily in laboratory leach studies. A series of cold runs were made with ratios varying from 5.5 to 7.0 lb/gal to determine their handling qualities. At 7 and 6.5 lb/gal the grouts were very thick and it was difficult to prepare leach samples without bubble or other surface flaws. At 6 lb/gal the grout was pourable and produced acceptable solids for leach testing. Results from a grout made at 5.5 lb/gal showed it would also be acceptable but the higher ratio

(6 lb/gal) was chosen. Phase separation was low at both ratios, 0.63% and 0.47% at 5.5 and 6.0 lb/gal, respectively.

Leach samples were prepared from the aforementioned grouts by pouring them in 6 oz plastic bottles that had been cut off 50 mm from the bottom. Thus as in the IAEA requirements the leach samples will be 50 mm in dia and 50 mm high. A total of about 100 cm^3 of grout was in each sample. A surface area of 20 cm^2 will be exposed to the leachant. The samples were cured 7 days by placing the plastic containers in a tray of water inside a plastic bag. After curing each sample was placed in another container and 150 ml tap water added. The water was changed daily. The average pH of these leachant solutions decreased from 12.4 for the first 24 hr period to around 10 for the ninth 24 hr period. A small amount of flocculent ppt formed each time but this dissolved on the addition of 0.4 ml conc. HCl. Thus in the radioactive leach tests, samples of the leachant may be taken before and after the addition of a small amount of conc. HCl to determine if any activity is present in the precipitate. The cold tests were discontinued after 9 days and the samples examined. The grout fit tightly against the plastic. There was no evidence of any gap although it was possible to pry the plastic away from the grout. Since there was such a tight fit there will be no further treatment of any of the radioactive leach specimens prior to adding the leachant.

Activity in Phase Separated Water

A grout containing ^{85}Sr was prepared at 4 1/2 lb/gal to determine the percentage of activity that would be present in the phase separated water. There was 2.9% phase separation and the water contained 0.018% of the total activity. The grout was prepared using 200 ml of W-7 simulated waste solution containing 6.59×10^5 c/m/ml ^{85}Sr. Sufficient dry mix was added to produce a grout with a solids/liquid ratio of 4 1/2 lb/gal to insure enough phase separation liquid to measure. The grout was next poured into two 100 ml graduates and allowed to stand 2 hr. There was 2.9% phase separation in each test containing approximately 3.4×10^3 c/m/ml ^{85}Sr.

Variation of Grout Viscosity with Time

The viscosities of two identical grouts were measured on the Halliburton Thickening Time Consistometer over a period of 8 hrs to determine the effect of constant vs intermittent stirring. One grout sample remained on the consistometer for the entire period so it was being stirred constantly at 150 RPM. The viscosity decreased from 15 to 8 poises in the first half hour then increased to 10 poises at the end of 1 hr. It remained at this reading for 4.5 hr then slowly increased to a value of 14 at the end of the 8 hr period.

Readings were made on the second grout only every half hour with no stirring between readings. The viscosity remained constant for about 2.5 hr then increased to a value of 20 at the end of 4.5 hr. It remained around this value for the remainder of the test period. After the 7.5 hr reading it was left stirring on the consistometer. After 15 min the viscosity had decreased to 15 poises, only 7% higher than the grout which was stirred the entire period.

INJECTION ASSISTANCE

The rate of bleed-back of free water from the injection well following the completion of the recent series of injections was determined. It had been previously observed that the rate of bleed-back after Injection ILW-10 was strongly dependent on the length of time the well was shut-in before the measurements were made. A similar phenomena was noted for the bleed-back measurements after Injection ILW-11. The initial bleed-back rate was 5 gal/min at 9 days after the completion of the injection. After this rate was determined, the well was shut. The rate was redetermined at 24 days after the injection and at 45 days after the injection; these rates were 2.8 and 1.6 gal/min respectively. It is now planned to determine the rate again after several months shut-in time. At this time all of the remaining free water will be bled from the fracture.

The particular mechanisms responsible for this behavior of the bleed-back rate are not yet understood. The change in bleed-back rate with time closely parallels the curves for change in cement strength with time, but

the correlation may be merely fortuitous. More investigation of this phenomena is needed.